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ALKOXO-TECHNOLOGY OF NANO-MICRO-STRUCTURED SOLS FOR CERAMIC MATERIALS

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A method is proposed for synthesizing sol with controlled particle size by influencing the parameters of the hydrolytic polycondensation process. The possibility of synthesizing sols by changing the mass, time and temperature parameters of the hydrolysis reaction for tetraethoxysilane (TEOS) as well as a mixture of TEOS with a product of its partial hydrolysis — ethylsilicate-40 (ETS-40) — in the presence of an electrophilic or nucleophilic catalyst is studied. The particle sizes and distribution in the synthesized sample are determined.

Key words: ceramic, functional coatings, alkoxy-technology, sol, controlled structure, hydrolytic polycondensation, elemental alkoxides, alkoxysilane.

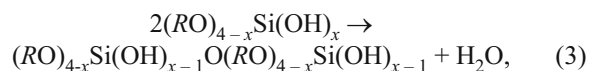
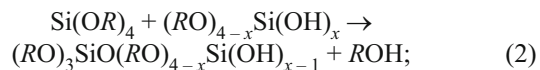
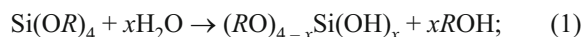
In terms of many physical properties — thermal stability, mechanical strength, resistance to aggressive media, high dielectric properties, optical and radio wave transparency, etc. — ceramic materials are irreplaceable in many fields of engineering.

One of the most promising methods of obtaining ceramic materials based on pure oxides is alkoxy-technology, based on the use of elemental alkoxides — alkoxides of different elements (Si, Zr, Hf, Ti, Al and others) — as initial materials [1].

The alkoxy-sol-gel method makes it possible to obtain high-purity sols and control the particle size and concentration, thereby securing a prescribed stoichiometric composition, which makes possible directed synthesis of different precursors for producing general and special purpose ceramic materials, including sols for obtaining functional coatings, reinforcing fibers and permeation of ceramic-matrix materials, aerogels, xerogels, nanopowders of complex oxides, fibers and many other products [2 – 9].

The present work is devoted to studying the possibility of synthesizing sols with controllable particle size by varying the mass and temperature-time parameters of the hydrolytic polycondensation (HPC) reaction of tetraethoxysilane (TEOS)

as well as mixtures of TEOS with products of its partial hydrolysis by ethylsilicate-40 (ETS-40). This choice of initial alkoxides was determined by the capacity of alkoxysilanes to form polymer siloxane structures in the process of HPC in the presence of nucleophilic or electrophilic catalysts [10], as a result of which the degree of hydrolysis and condensation can be controlled by changing the parameters of synthesis, thereby ensuring the formation of a prescribed sol structure. During HPC of alkoxides in the presence of nucleophilic catalysts hetero- (2) and homo- (3) condensation reactions lead the hydrolysis reaction (1) in terms of the reaction rate. The reaction scheme is presented here for the example silicon tetra-alkoxides:



where $R = -\text{CH}_3$ or $-\text{C}_2\text{H}_5$.

In summary, the HPC reaction in the presence of nucleophilic catalysts yields polymer alkoxysiloxanes with the minimal content of SiOH fragments. Conversely, in the case of HPC of alkoxysilanes in the presence of electrophilic

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TABLE 1. Effect of the Hydrolysis Method on the Sol Obtained

Experiment No.	Reagents		Hydrolysis method	Average size of sol particles (range), nm	Exterior appearance	Figure No.
	Alkoxysilane	Catalyst, %				
Alkaline hydrolysis						
1	TEOS	Ammonia 1.2*	Direct slow	19.3 (10.7 – 85.9 nm)	Strong opalescence ("moonstone")	1
2	TEOS	Ammonia 1.2*	Direct fast	2.8 (1.6 – 5.4)	Weak opalescence	2
3	TEOS	Ammonia 1.2*	Reverse slow	5.1 (3.2 – 21.5)	Weak opalescence	3
4	TEOS	Ammonia 0.6*	Direct slow	6.5 (4.5 – 43.0)	Transparent	4
5	Mixture of TEOS and ETS-40	Ammonia 0.6*	Direct slow	65.1; 190; 500 (43 – 6500)	Strong opalescence	5
Acidic hydrolysis						
6	TEOS	HCl 0.05*	Direct slow	2.69 (1.6 – 7.6)	Transparent	6
Alkalkine hydrolysis. Intensified condensation of sol						
7	TEOS	Ammonia 1.2*	Direct slow	110 – 440; 2700; 5700 (50 – 6500)	Strong opalescence ("moonstone")	7

* Content of the catalyst in the reaction mass, %.

catalysts alkoxysilanes with a high content of SiOH fragments are formed, since in this case the hydrolysis (1) leads the condensation reactions (2) and (3). For this reason, the reaction should be conducted in a water-alcohol solution in order to slow down the hydrolysis reaction, since untimely accumulation of large quantities of SiOH groups in the reaction mass can lead to gel formation. To obtain sol the HPC of alkoxysilanes in acidic and alkaline media must be conducted with excess water in order to shift the equilibrium (1), (2) and (3) rightward and allow all alkoxy groups to participate in the hydrolysis-condensation reactions.

EXPERIMENTAL PART

Analytical grade TEOS, ethyl silicate ETS-40 (GOST 26371–84, rev. 1 – 2, highest grade) and grade A absolute ethyl alcohol were used in the present work.

An ammonia solution, obtained from a 25% water solution of NH_3 (technical grade A ammonia solution, GOST 9–92) and distilled water, was used as the nucleophilic catalyst. In the experiments the ammonia content was varied from 0.6 to 1.2% and in the HPC process the pH of the medium was 9 – 11. The TEOS concentration in the solution was 0.71 mole/liter and the mass content of the solid phase in the synthesized alkaline sols fluctuated in the range 4.00 – 4.25%.

A mixture comprised of TEOS and the product of its partial hydrolysis ETS-40 was obtained by mixing reagents in the mass ratio 49 : 1, respectively. The TEOS concentration in the solution was 0.71 mole/liter and the content of ammonia in the reaction mass was 0.62%.

Alkaline sols based on TEOS were produced in a four-neck flask equipped with a mixer, thermometer, drop-

ping funnel, reflux condenser and water bath. Synthesis was conducted using direct (TEOS in the column, ammonia solution in the dropping funnel), reverse (ammonia solution in the column, TEOS in the dropping funnel), slow (to 10 ml/min) and fast (about 40 ml/min) input of the reagents with the temperature of the reaction mass increasing from 25 to 37°C owing to the reaction heat. In all experiments in this series, at the completion of drip-in the mass was mixed for 24 h, and in the process the temperature decreased evenly from the maximum value to the initial temperature 25°C (the temperature of the water bath). Intensified condensation of the products of hydrolysis was conducted in some experiments by removing the highly volatile products of reaction. The process was conducted by using a rotary film evaporator (residual pressure 0.095 MPa, temperature 20 – 25°C) to mass fraction of nonvolatile substances at least 28%, creating a vacuum with the aid of a water-jet pump.

An alkaline sol based on a mixture of TEOS and ETS-40 was obtained by using direct slow input (about 7 ml/min) of the hydrolyzing agent. The maximum temperature of the synthesis reaction was 32°C.

A chemical grade 36% hydrochloric acid solution (GOST 3118–77) was used as the electrophilic catalyst. The pH in the medium during the HPC process was 1 – 3.

The TEOS-based acidic sol was obtained as follows. First, an acidic water-ethanol mixture with molar ratio of the components 1 part water to 2.55 parts ethanol (the content of acid in this mixture was 0.15%) was prepared. Next, TEOS and ethanol in the molar ratio 1 : 1.4, respectively, were loaded into a four-neck flask equipped with a mixer, thermometer, dropping funnel, reflux condenser and water bath, and the mass obtained was mixed for 5 min. Then an acidic water-ethanol mixture was added in drops from the dropping

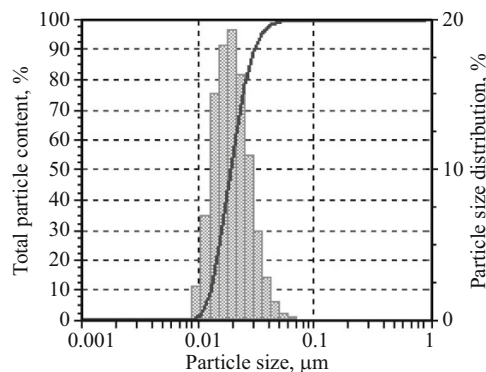


Fig. 1. Alkaline silica sol based on TEOS: experiment 1 (see Table 1).

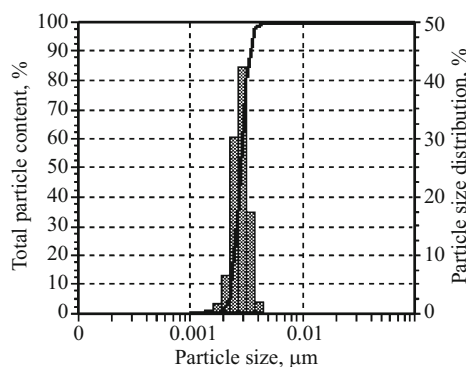


Fig. 2. Alkaline silica sol based on TEOS: experiment 2 (see Table 1).

funnel into the reaction mass in the flask; the input rate was about 2 ml/min. The acid content in the reaction mass was 0.05%. The input of the hydrolyzing agent was started at temperature 25°C, and because of the exothermal effect the temperature of the reaction mass increased to 42°C. After the input of the acidic mixture was completed the contents of the flask were mixed for 24 h and in the process the temperature evenly decreased from the maximum value to the initial temperature 25°C (the temperature of the water bath).

The sols obtained in this manner were studied with the aid of a Nanotrak ULTRA 253 particle size analyzer (Microtrac Co.) with measurement range 0.8 – 6500 nm and laser diode with wavelength 780 nm.

DISCUSSION

The data obtained in these experiments are presented in Table 1.

The results obtained with the Nanotrak ULTRA 253 particle size analyzer are illustrated by a histogram and an integral curve (Figs. 1 – 7), which can be used to determine the average size of the particles and the particle size range and distribution.

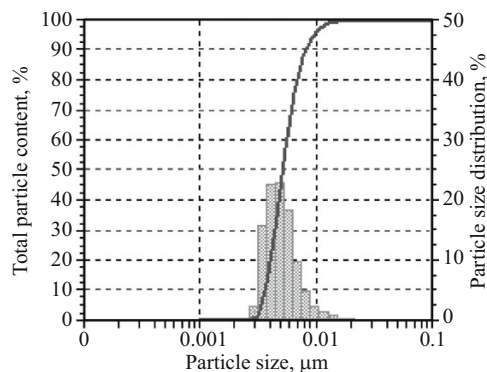


Fig. 3. Alkaline silica sol based on TEOS: experiment 3 (see Table 1).

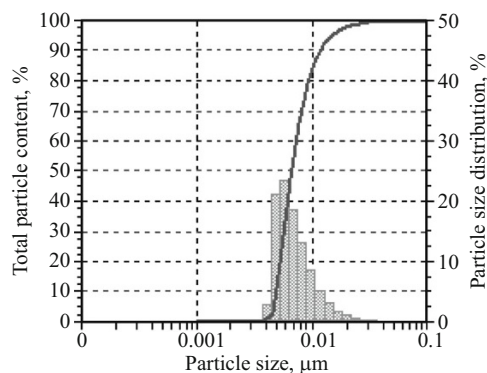


Fig. 4. Alkaline silica sol based on TEOS: experiment 4 (see Table 1).

In obtaining alkaline silica sols the particle size can be controlled by the rate at which the ammonia solution is input into the reaction mass. Slow input of the hydrolyzing mixture yields sols with particle size 10.7 – 85.9 nm (experiment No. 1, Fig. 1), which is larger than in the case of fast input of reagents (particle size 1.6 – 5.4 nm; experiment No. 2, Fig. 2). Fast input with the same temperature-time and concentration-mass parameters of the reaction yields silica sols with much smaller particles.

The order in which the reagents are added also plays an important role in sol formation. Thus, comparing the sol obtained with direct input of the reagents (experiment No. 1) and the sol obtained by adding TEOS to an ammonia solution (experiment No. 3, Fig. 3) shows that when the hydrolyzing mixture is added in the reverse order, other conditions remaining the same, particles with diameter 3.2 – 21.5 nm are formed, while in the case of direct input the size of the particles formed during synthesis is in the range 10.7 – 85.9 nm. Thus, large particles are formed when the ammonia solution is added to alkoxysilane.

A change in the ammonia concentration strongly affects the size of silica gel particles. For the same temperature, time and input rate of the reagents but with half the catalyst concentration sols with a different particle size distribution are

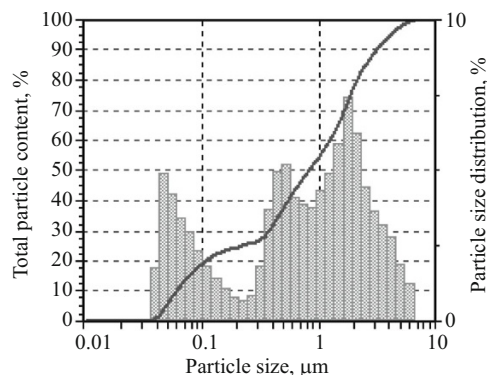


Fig. 5. Alkaline silica sol based on TEOS: experiment 5 (see Table 1).

obtained. The particle distribution in a sol obtained with a lower ammonia fraction (0.6%) compared with the sample obtained in the experiment No. 1, where the ammonia content was 1.2%, is presented in Fig. 4. As the mass fraction of the catalyst decreases from 1.2 to 0.6% the particle size decreases from 10.7 – 85.9 to 4.5 – 43.0 nm.

The particle distribution in a sol (experiment No. 5) obtained by alkaline hydrolysis based on TEOS and ETS-40 with 0.6% catalyst and fast input of reagent is presented in Fig. 5. As this figure shows, when a small amount of ETS-40 (partially hydrolyzed TEOS) is introduced into the reaction as an additional precursor, a nano- and microstructured sol is formed in the synthesis process; this is indicated by the particle size distribution function with maxima at 65.1 nm, 1.9 μm and 0.5 μm.

In the case of the TEOS-based acidic silica sol obtained with slow directed input of the reagents the mass fraction of the electrophilic catalyst HCl is 0.05%. The particle size range is 1.6 – 7.6 nm (experiment No. 6, Fig. 6).

When HPC is intensified it becomes possible to obtain nano-micro-structured sols in the process of concentrating the sol (experiment No. 7, Fig. 7) obtained by direct slow input with ammonia mass fraction in the reaction mass 1.2%, as indicated by the shift of the particle size into the micro range 0.05 – 6.5 μm and by the polymodality of the distribution curve with peaks appearing at 0.11, 0.44, 2.7 and 5.7 μm.

The data presented above show that the particle size in the sol obtained can be controlled by changing the nature and concentration of the catalyst as well as the order and rate of input of the reagents. Nano-micro-structured sols can be obtained by shifting the equilibrium of the HPC reaction toward intensified condensation due to removal of the low-molecular products of reaction and by using the products of the partial condensation of TEOS as additional precursors.

In summary, the alkoxo-technology made the following possible:

- the main parameters affecting the formation of particles with the required size were determined;

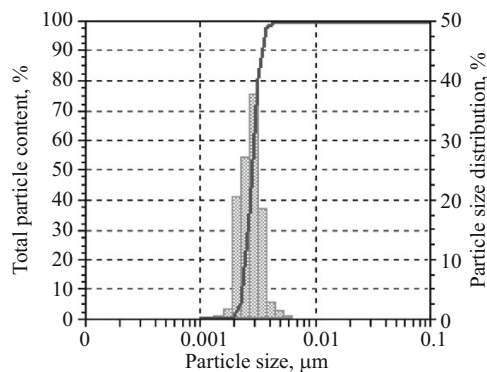


Fig. 6. Alkaline silica sol based on TEOS: experiment 6 (see Table 1).

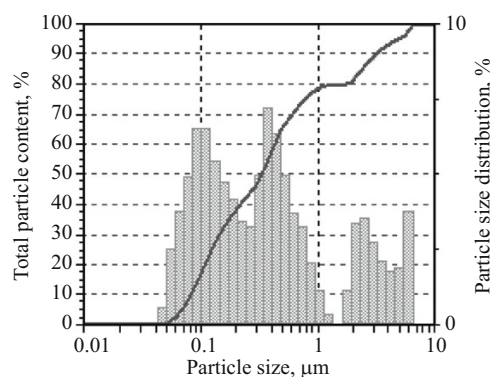


Fig. 7. Alkaline silica TEOS-based sol condensed to 30% nonvolatile substances: experiment 7 (see Table 1).

- it was shown that the nature and concentration of the catalyst and the order and rate of input of the reagents play an important role in the formation of sols with prescribed particle size;

- approaches to the synthesis of sols with controlled structure, including methods of obtaining nano-micro-structured sols as precursors for obtaining ceramic materials, were developed.

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